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AND SALES

2004905662 24 Sep 2004

AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION

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INVENTION TITLE: **Light sensitive/emitting device with improved performance**

Light sensitive/emitting device with improved performance

TECHNICAL FIELD

This invention relates to the thin film photovoltaic devices and sensors, materials and methods used for electrical connections for such devices, in particular, to materials and methods used for fabrication of such devices,

More particularly this invention relates to the nano-particulate photo-electrochemical (PEC) devices including sensors and photovoltaic cells. Examples of the nano-particulate PEC devices are disclosed in the following patents and applications:

US4927721, Photoelectrochemical cell; Michael Graetzel and Paul Liska, 1990.

US5525440, Method of manufacture of photo-electrochemical cell and a cell made by this method; Andreas Kay, Michael Graetzel and Brian O'Regan, 1996.

US6297900, Electrophotochromic smart window; Gavin Tulloch and Igor Skryabin, 2001.

PCT/AU01/01354, UV sensors and arrays and methods to manufacture thereof, George Phani and Igor Skryabin

BACKGROUND TO THE INVENTION

PEC cells, as of the type disclosed in the above patterns, are capable of being fabricated in a laminate arrangement

between two large area substrates without undue expense. One typical arrangement involves two glass substrates, each utilising an electrically conducting coating upon the internal surface of the substrate. Another typical arrangement involves the first substrate being glass or polymeric and utilising an electrically conducting coating upon the internal surface of the substrate, with the second substrate being polymeric. In some arrangements, the internal surface of said second polymeric substrate is coated with an electrically conducting coating, whereas in other arrangements, said second polymeric substrate comprises a polymeric foil laminate, utilising adjacent electrically conductive material, such as carbon. Also, in some arrangements, the external surface may be a laminated metal film, and in other arrangements, the external surface may be coated by a metal. At least one of said first and second substrates is substantially transparent to visible light, as is the attached transparent electrically conducting (TEC) coating. PEC cells contain a photoanode, typically comprising a ruthenium dye-sensitised, nanoporous semiconducting oxide (eg. titania) layer attached to one conductive coating, and a cathode, typically comprising a redox electrocatalyst layer attached to the other conductive coating or conductive material. An electrolyte containing a redox mediator is located between the photoanode and cathode, and the electrolyte is sealed from the environment. If one or more polymer substrates are utilised, the photoanode and the cathode are typically electrically separated by a porous insulating layer (eg. insulating ceramic oxides) or spacer(s) (eg. insulating spheres). TEC coatings, which usually comprise a metal oxide(s), have high resistivity when compared with normal metal conductors, resulting in

high resistive losses for large area RPEC cells operating under high illumination. When operating under high illumination, one method to minimise these losses is the deposition of one or more networks of electrically conductive material that serve to collect and/or distribute electrons in the cell. Another method to minimise these losses is by connecting a multiple of PEC cells (here called 'PEC modules') in series to generate higher voltages and to minimise total current. Such connections in RPEC modules may be made externally or internally (International Application PCT/AU00/00190). To enable internal series connection of adjacent RPEC cells, selected areas of such conducting coatings must be electrically isolated, portions of such areas overlapped when laminated, interconnects used to connect such overlapped areas and electrolyte-impermeable barriers used to separate the electrolyte of individual cells.

One example of the manufacture of an PEC module involves the use of two glass substrates that have TEC-coatings that have been divided into electrically isolated regions. Titanium dioxide (or similar semiconductor) is screen printed onto selected areas of the TEC coating of one substrate and an electrocatalyst is screen printed onto selected areas of the TEC coating of the other substrate. The titanium dioxide (titania) is coated with a thin layer of a dye by immersion of the titania-coated substrate in the dye solution. Strips of sealant and interconnect material are deposited upon one of the substrates and the two substrates are then bonded together. Electrolyte is added to the cells via access apertures in one of the substrates and these apertures are then sealed.

Another example of the manufacture of an PEC module involves the use of one substrate with a TEC-coating that has been divided into electrically isolated regions. Successive layers of titania, insulating ceramic oxide, and conducting catalytic material (for example, carbon-based) are deposited, for example by screen printing, onto selected areas of the TEC-coated substrate, with the catalytic layer also serving as an interconnect. The titania is coated with a thin layer of the dye by immersion of the multiple-coated substrate in the dye solution. Electrolyte is added to the spaces within the porous titania-insulator-catalytic layers. The sealant face of a sealant/polymer and/or metal foil laminate is sealed to the substrate.

One advantage of PEC devices described above is in better than of conventional sold state device angular performance. It has been demonstrated that these devices perform well even under diffuse light conditions or when solar angle of incidence differs from normal. This advantage is attributed to nano-particultate structure of photo-active layers, that provides high area of photoactive surface. Each nano-particle, coated with thin layer of dye absorbs light incident from all directions, thus improving angular performance for a whole cell.

Unfortunately, these advantages of PEC are reduced by necessity of utilizing substantially planar substrates. An interface between a planar substrates and air reflects significant part of solar energy at low angles of incidence. Antireflective coatings could overcome this problem only partially; their antireflective properties

are typically wavelength dependent, thus optimized for only small part of solar spectra.

In addition, the said PEC devices, especially of large size require highly conductive and simultaneously transparent coating. Electrical resistance of transparent electrical conductors is often a limiting factor for performance of devices larger than 5-10mm.

OBJECTIVES OF THE INVENTION

It is therefore an object of the present invention to provide a thin film PV device, more particularly a Photoelectrochemical with improved performance by minimizing ohmic losses on transparent conductor and improving utilization of light at high angles of incidence.

SUMMARY OF THE INVENTION

The invention provides for the PEC cells to be formed in substantially spherical shape, attached to local predetermined regions of support plate.

To minimize ohmic losses in transparent conductive coatings each sphere is made relatively small.

Although, this specification describes shape of PEC cell as spherical, the invention is not limited to geometrical spheres, but provides for other, substantially curved and not necessary regular shapes and/or sections or partitions of the sphere.

From one aspect of invention the PEC cell comprises spherical electrically conductive core, on which layers of

the PEC cell are sequentially deposited. The top, electrically conductive layer comprise any of known transparent electrically conductive materials including, but not limited to

Transparent conducting oxides,
Conducting polymers,
Mesh made of conducting fiber.

The invention provides for a hole to be made in at least external layer of the PEC device to enable external electrical connection(s) to the device. In one embodiment the conducting coating is extended to coat all or part of the internal surfaces of said hole(s) and provide said external electrical connection(s) and whereby said hole(s) are filled with the same or a second electrically conductive material or non-conducting material (e.g. ceramic glaze), forming a bond with said conducting coating and sealing said hole(s);

This invention provides for electrical connections to be made to said electrically conductive coating (including TEC) and/or to said electrically conductive material (ECM) via holes in one or both of the substrates, thereby eliminating the need for said electrically conductive coating and/or said electrically conductive material to penetrate the hermetic seal of RPEC cells and modules.

One layer of the said device comprises semiconductor. For wide band gap semiconducting materials invention provides for photosensitization by dye, to absorb electromagnetic energy of light. It is preferably to utilise nano–

dispersed semiconductors, thereby significantly increasing photoactive area of a cell.

In one embodiment layers of a cell are formed on internal surface of transparent spherical shape. The shape being made of glass, polymer or any other material transparent to the part of electromagnetic radiation that is absorbed by either dye when photoactive material comprise a dye attached to a semiconductor or just by semiconductor in absence of dye. Depending on application the part of the electromagnetic radiation comprise UV light, visible light, IR light or any combination thereof.

In another embodiment, the layers of PEC device are formed on the spherical electrically conductive core, the last layer being optically transparent. The said core is selected from metallic (Ti, W, SS, etc) or non-metallic (carbon, conductive polymers, etc.) conductors.

The invention provides for the spherical PEC cell to be connected to support plate by standard connecting means utilised in PCB technology. For the purpose of connection (both electrical and mechanical) the invention provides for electrically conductive pin, embedded into the PEC cell. In case of double sided PCB the invention provides for utilization of a hole in PCB for the back side connection.

The invention provides for using mirror-like plate or for deposition of highly reflective layer on top of the said supportive plate.

It could be beneficial to place more than one spherical cell on the same supportive plate and electrically interconnect them using standard PCB means. The invention also provides for a flexible supportive plate, when flexibility is required.

The invention also provides for using an internal space of a spherical device as an additional reservoir for electrolyte and drying agents. Additional electrolyte will extend useful life of the device by replacing lost or damaged electrolyte layer adjacent to the semiconducting layer. The semiconducting layer may or may not be covered by dye.

According to another aspect of the invention a plurality of spherical cells is formed on conducting mesh.

According to still further aspect, the invention provides for utilization of light emitting layers, preferably layers of organic light emitting diodes in place of photovoltaic cell described above.

BRIEF DESCRIPTION OF DRAWINGS

Having broadly portrayed the nature of the present invention, embodiments thereof will now be described by way of example and illustration only. In the following description, reference will be made to the accompanying drawings in which:

Figure 1 is an enlarged section of a spherical PEC cell formed in accordance with one example of the invention.

Figure 2 is an enlarged section of a spherical PEC cell formed in accordance with second example of the invention.

Figure 3 is an enlarged section of a spherical PEC cell formed in accordance with third example of the invention.

Figure 4a is an enlarged section of 2 spherical PEC cells formed in accordance with fourth example of the invention.

Figure 4b is an enlarged section of 4 spherical PEC cells formed in accordance with fourth example of the invention.

Figure 5 is a 3D representation of a surface covered by spherical PEC cells.

Figure 6a is a planar view of a flexible system that comprises plurality of spherical cells formed in accordance with 5th example of the invention.

Figure 6b is an enlarged partial section of a system formed in accordance with 5th example of the invention.

Figure 7 is an enlarged partial section of a spherical cell formed in accordance with 6th example of the invention.

Detailed description of drawings.

Referring to Fig.1 a layer of dye-sensitised nano-particulate TiO_2 (about 10 micron thick) is formed on a conductive core (Titanium). A porous ceramic layer (zirconia), filled with electrolyte surrounds the said layer of nano-particulate TiO_2. The porous layer is followed by a layer of conductive catalytic polymer, connected to a positive terminal. To form a negative terminal a conductive pin connects the conductive core to a terminal on the opposite side of a support.

Referring to Fig. 2 a spherical PEC device is formed on internal surface of a hollow glass sphere. A hole premade in the sphere serves both for depositions of layers and for connecting a final device to external electrical terminals. Subsequent layers of transparent conductor, dye sensitised TiO_2 and porous ceramic insulating material are deposited on internal surface of the sphere. The transparent conductor layer is extended to cover walls of the hole and part of external surface of the sphere. An electrolyte is added to the porous insulating material. After deposition of the layers a remaining space inside the sphere is filled with carbon based material that serves as a counter electrode for the PEC device. A conductive pin is secured in carbon layer. Sealing of the hole ensures that humidity and oxygen from environment could not penetrate inside the device. Additionally the sealing prevents evaporation of the electrolyte. The device is secured on a support (flexible or rigid). Spring loaded connectors ensure good electrical connections between the device and external electrical terminals. To enhance light capturing property a mirror is placed underneath the device on top of the support. A hole

made in the support provides for connection of conductive pin to the spring loaded terminal placed on the bottom side of the support.

Referring to Fig.3 a spherical device formed similarly to the device of previous example. Instead of a pin, a conductive core is extended to outside of the sphere to provide electrical connection to a positive terminal formed on a top surface of a support by deposition of a conducting coating to predefined areas of the support. Negative terminal is connected to to a a device conducting layer extended to the walls of a hall in the sphere and to external surface of the sphere. A sealant applied externally provides impermeable barrier between the device and environment and additionally adheres both to the sphere and to the support, thus securing the device on the support.

Referring to Fig.4a each spherical device is located at point along the mesh centers. The mesh centers occur periodically at points where strands of wire running lattitudinally meet with strands of wire running longitudinally. The mesh may be made from example, titanium or tungsten wire. Each cell is built on around a spherical and catalytic center located at each mesh center. The catalytic core can be made of for example carbon or graphite or other catalytic materials such as Platinum. The catalytic core is coated with an insulating porous shell structure made of for example a zirconia or polymer material. The insulating material is then coated with a shell of Titanium dioxide, which itself is coated in a light absorbing dye. An electrolyte (polymer gel or liquid) is then allowed to penetrate the porous sphere through to the catalytic core. The entire sphere is then

coated with a transparent conducting polymer that protects the cell from external environmental effects such as moisture or UV light. (Protection from UV-light is not required when the device is formed to be a UV sensor. In this case no dye is applied to the semiconductor). Electrical connections may be made externally along the mesh cutoff point. The entire mesh/sphere layout can be processed in a continuous in-line flexible roll.

Referring to Fig. 4b and enlarged part of the system described in the previous example is shown.

Referring to Fig. 5 a 3D surface on which multiple spherical devices will be formed is shown. Proposed "Egg Cup" profile, is similar to known designs of DSC with the exception of the profile. Flat edges allow for the possibility of interconnects, or external connection. The profile provides for a significant increase in the collected light due to capturing light from internal reflections that would otherwise be reflected from the interface between air and surface.

Referring to Fig. 6a a plurality of spherical cells are formed an a flexible non-conductive base, Each cell comprises a metal dome, a counter electrode, an electrolyte, a working electrode and a molded conducting cover. Embedded electrical connectors provide for parallel and series connections of the cells. The above diagram shows the DSC Domes connected in parallel along the Y Axis and connected in series along the X Axis. Also the above configuration implies any form of 3D Polygon for more complete coverage of the non-conductive base.

Referring to Fig. 6b a cross sectional view of a previous example is shown.

Referring to Fig. 7 is a cross-sectional view of a one cell photovoltaic device formed on a conductive (e.g.

metal) core. The base of the conductive core and a conductive pin are coated by an insulating thermoplastic. The crown of the sphere is coated by a counter electrode catalytic layer and subsequently covered with a porous insulating layer to prevent short-circuiting between a working and counter electrodes. The external skin is a conductive mesh coated by a thermoplastic. A dye sensitised TiO_2 layer is formed on the conductive mesh. The electrolyte is placed on the TiO_2 layer. The crown of the conductive metal sphere is placed into the electrolyte and the conductive mesh/TiO_2 layer forming an indent in the external skin. The skin is enveloped around the base pin of the conductive sphere and heat-sealed thus forming a bladder of electrolyte at the base of the sphere in such a way that photoelectrons generated in the TiO2 layer are transferred without large ohmic losses. The positive and negative electrodes from the cell are the metal conductive pin and the conductive mesh respectively._This invention also allows for the inversion of the counter and working electrodes.

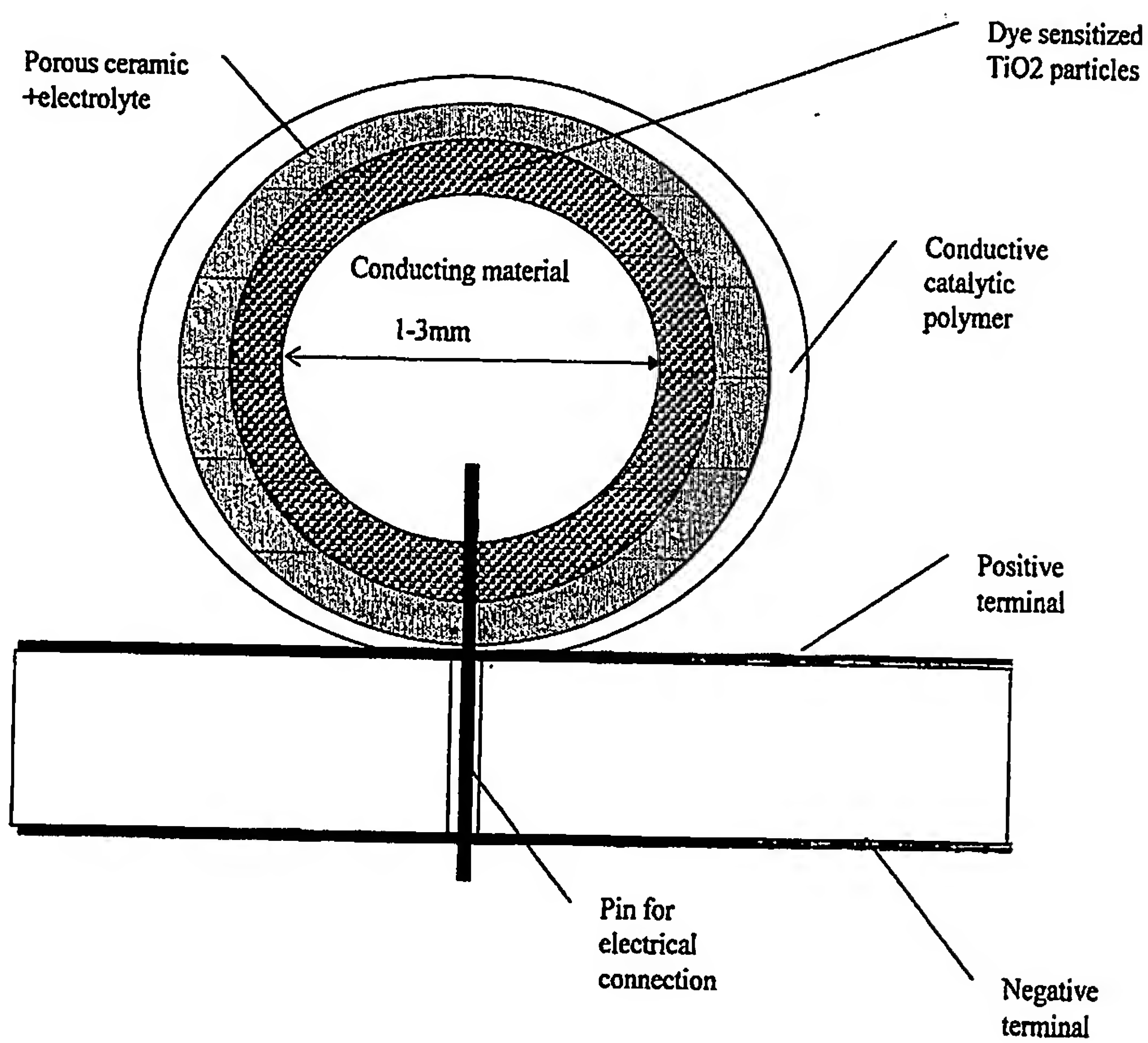
Porous ceramic
+electrolyte
Dye sensitized
TiO2 particles
Conducting material
1-3mm
Conductive
catalytic
polymer
Positive
terminal
Pin for
electrical
connection
Negative
terminal

Figure 1

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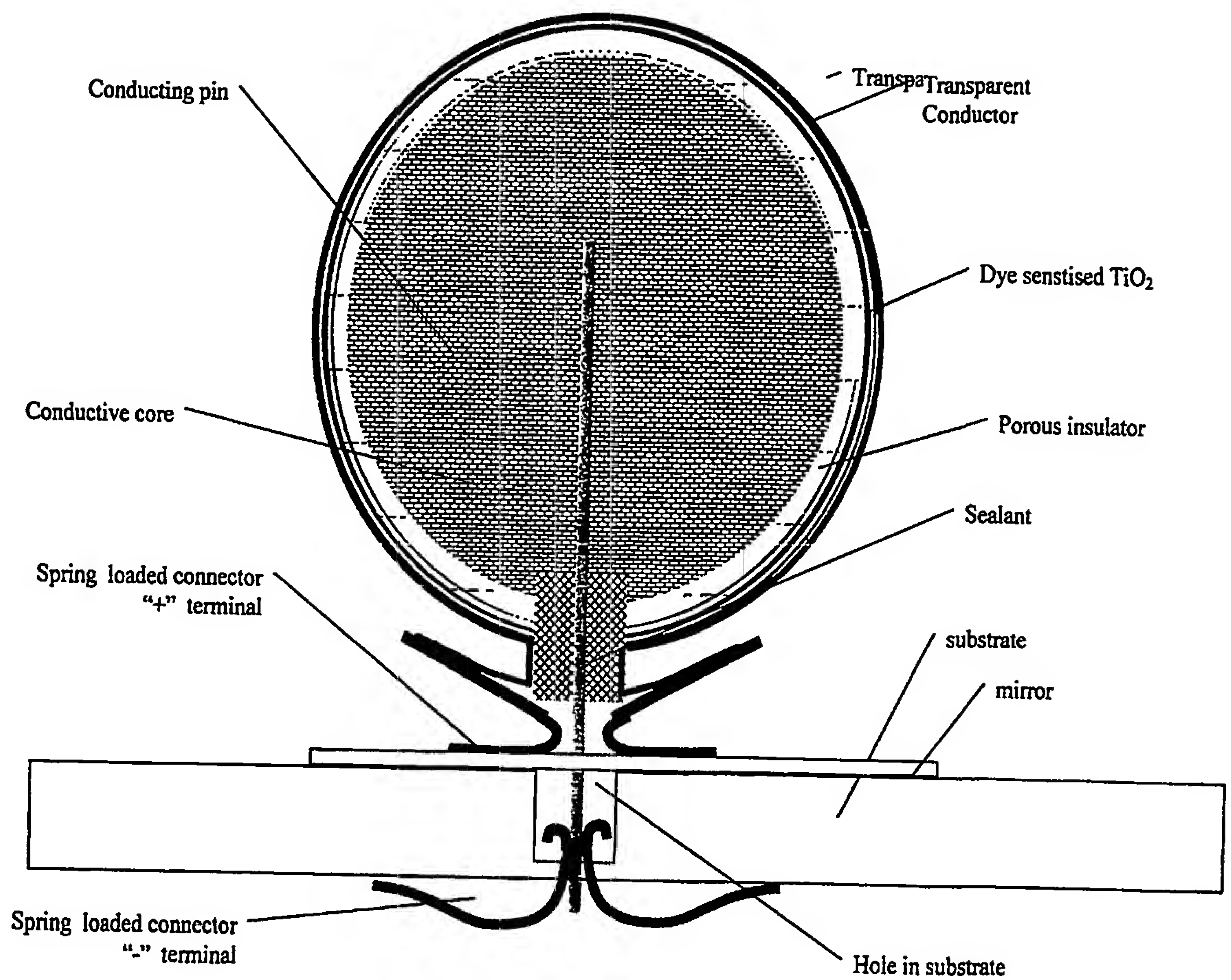

Figure 2

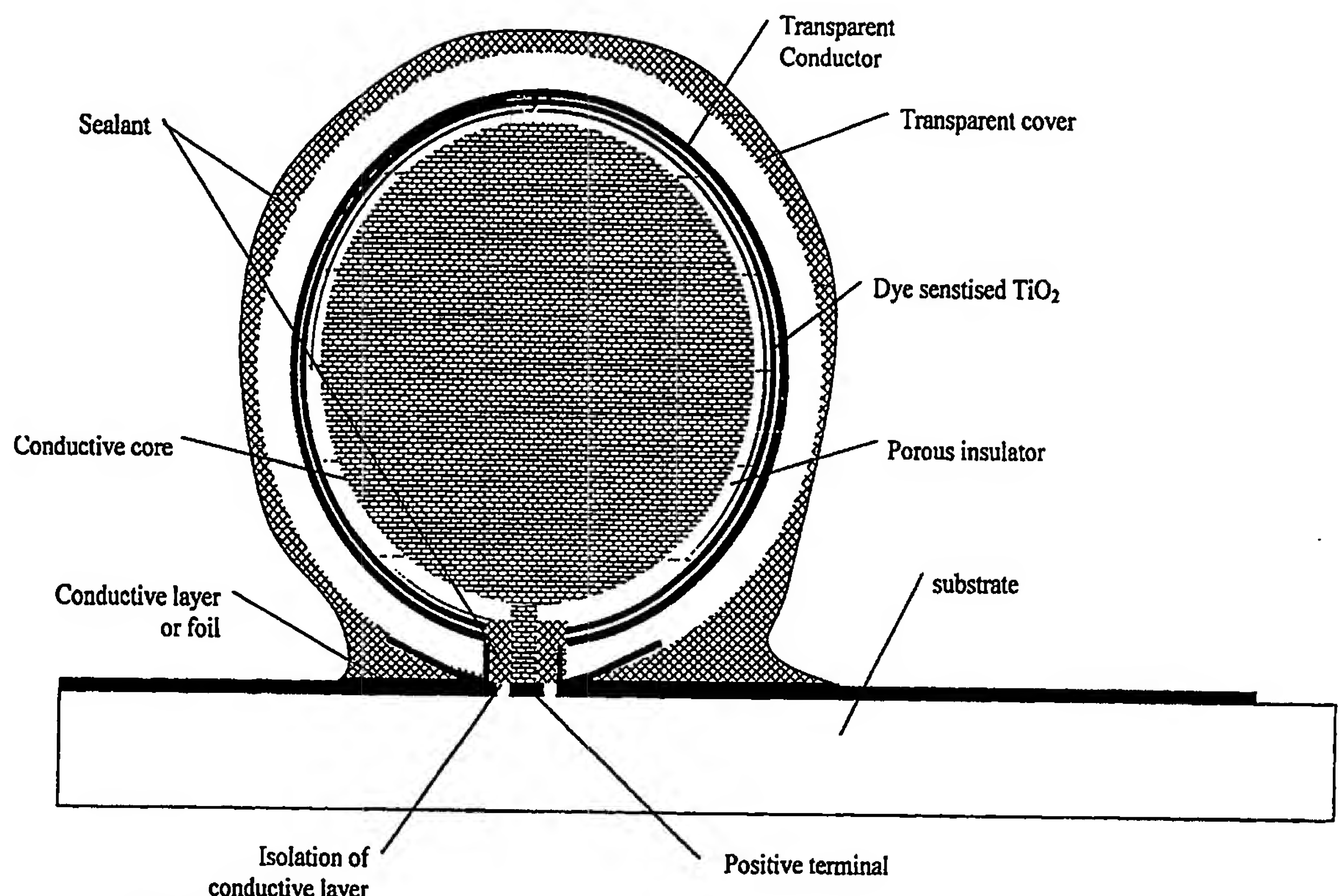
Transparent
Conductor
Sealant
Transparent cover
Dye senstised TiO_2
Conductive core
Porous insulator
Conductive layer
or foil
substrate
Isolation of
conductive layer
Positive terminal

Figure 3

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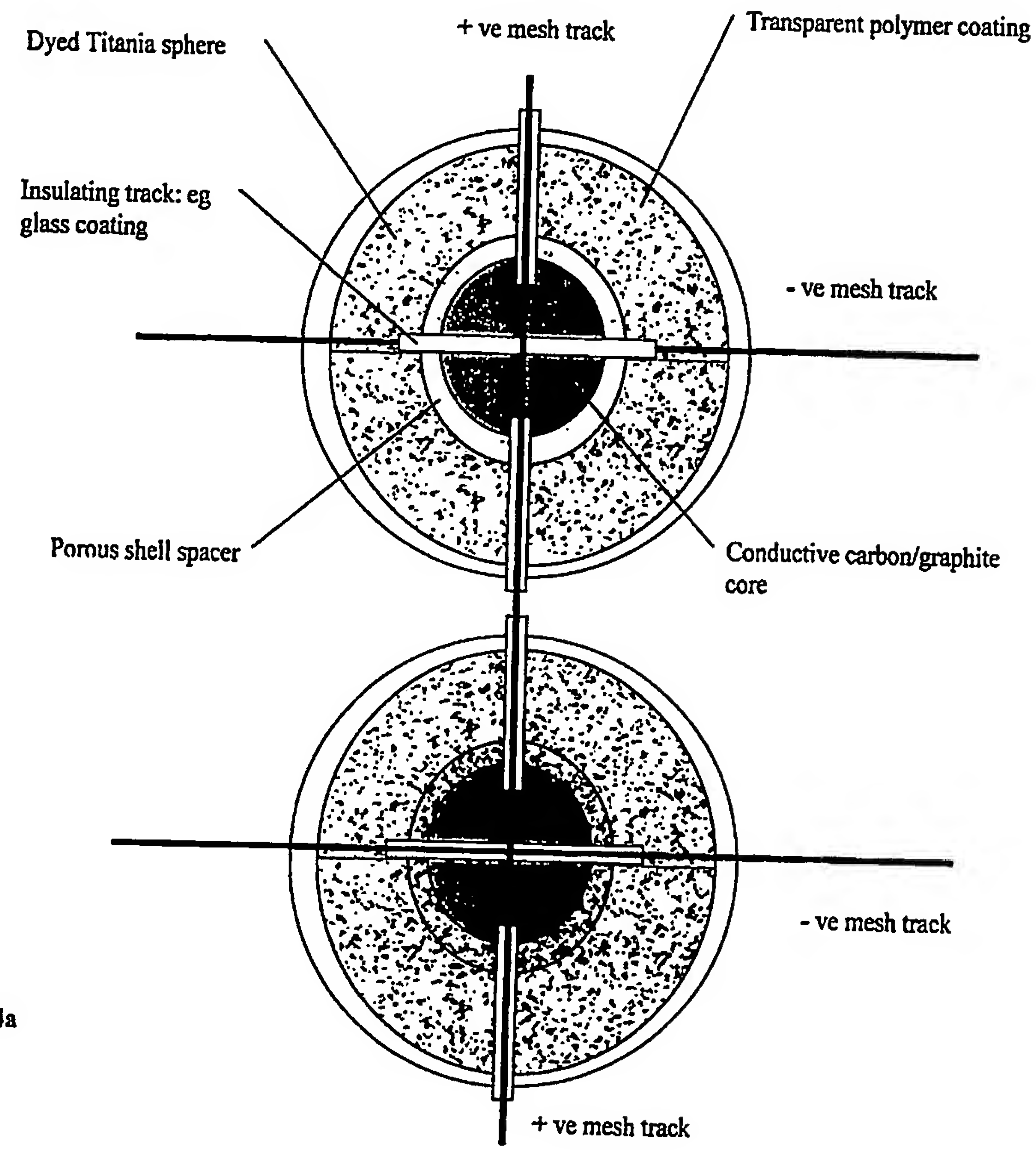

Figure 4a

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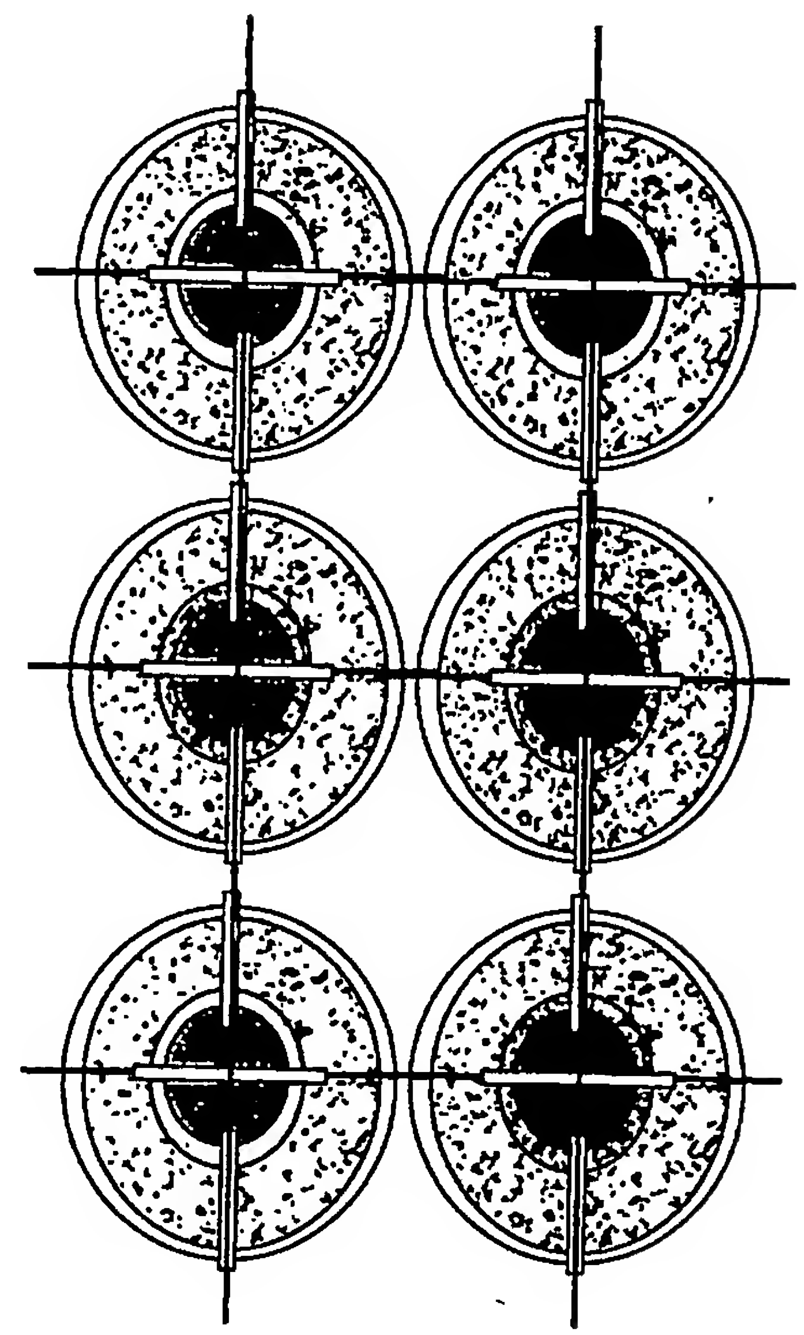

Figure 4b

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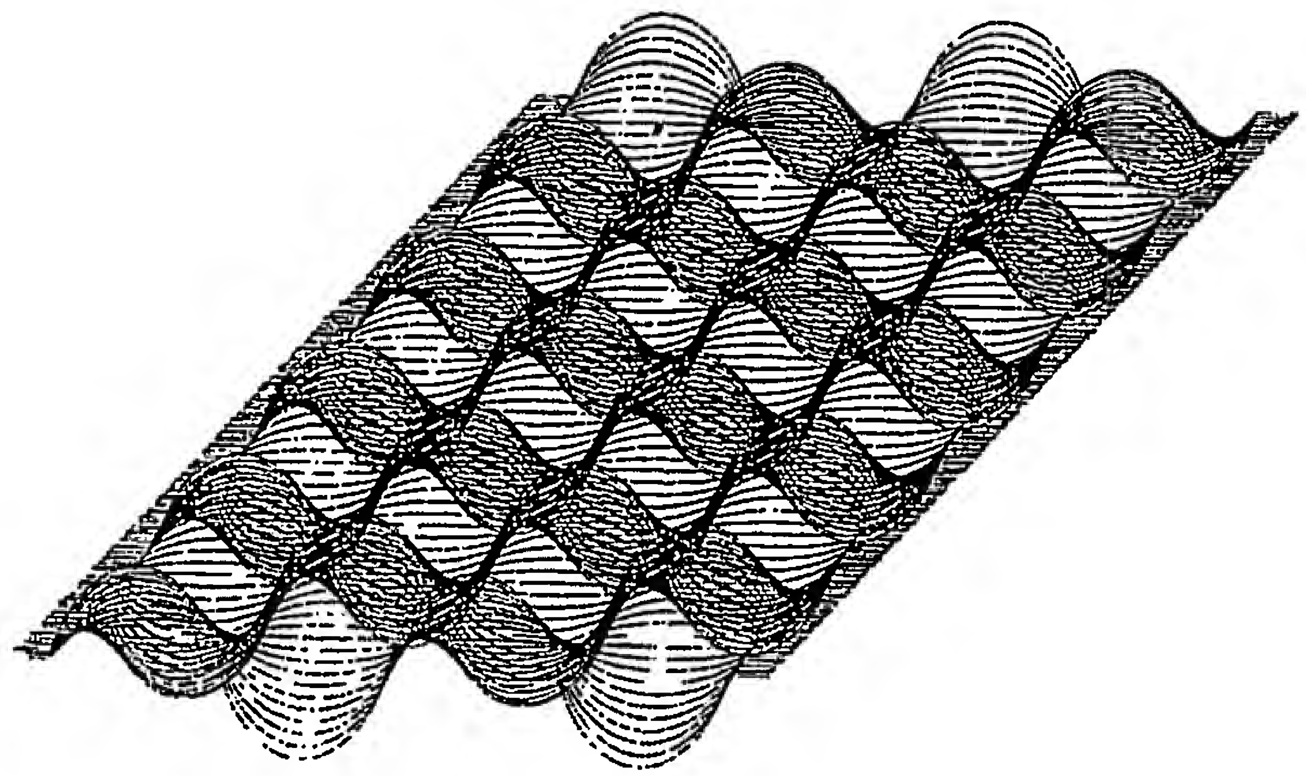

Figure 5

- Metal Dome
- Counter Bectrode
- Bectrolyte
- Working Bectrode
- Molded Conducting Cover
- Embedded Bectrical Connections
- Flexible Non-Conductind Base

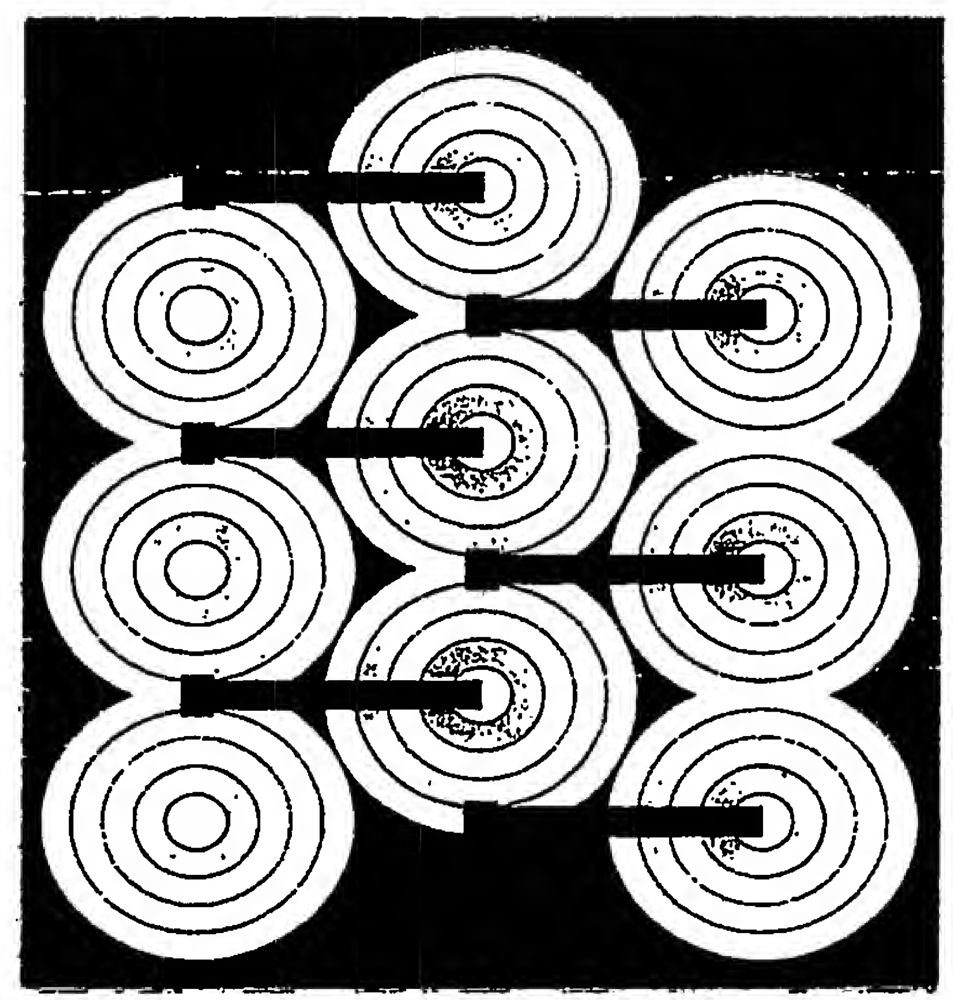

Figure 6a

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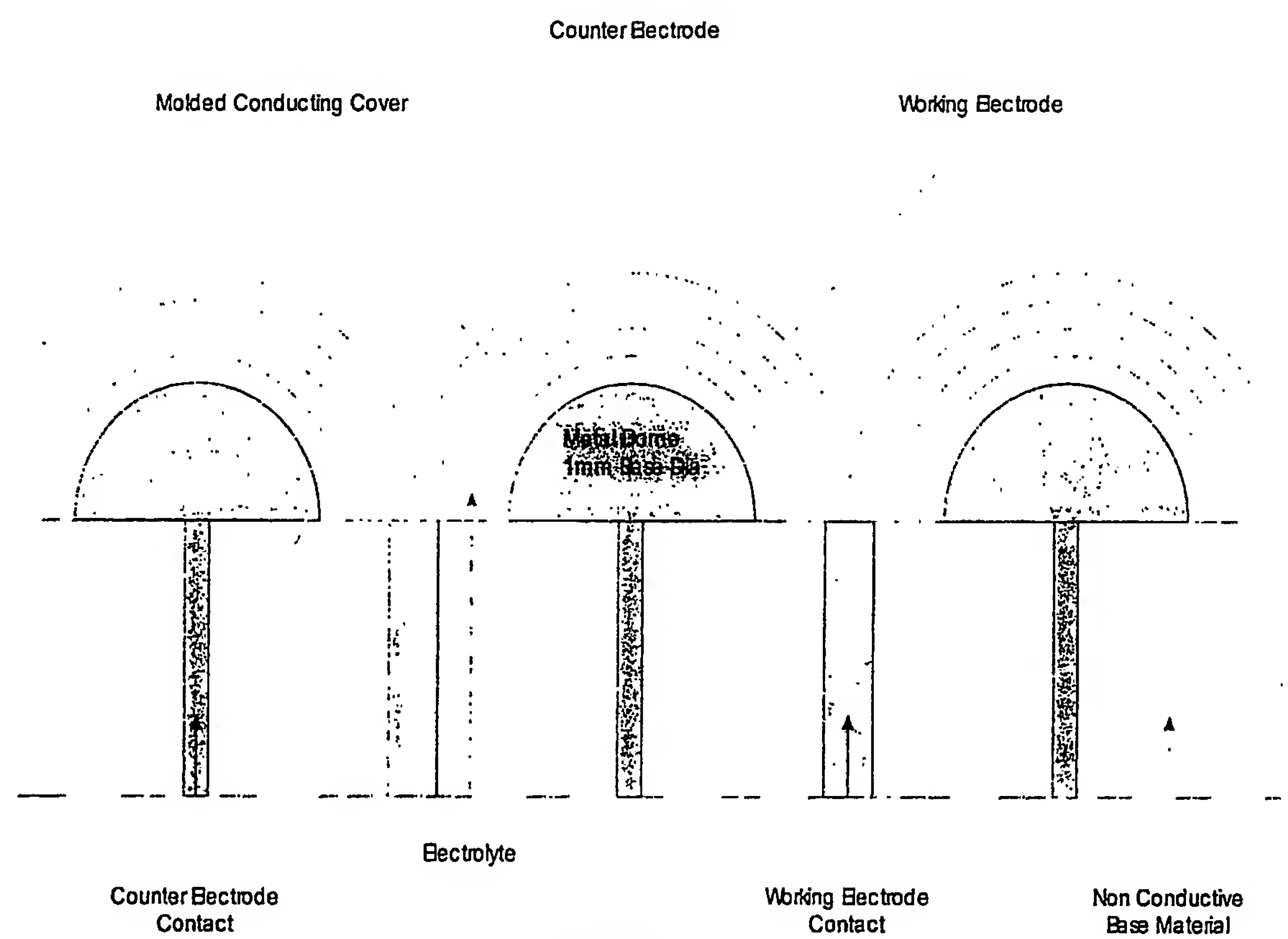

Figure 6b

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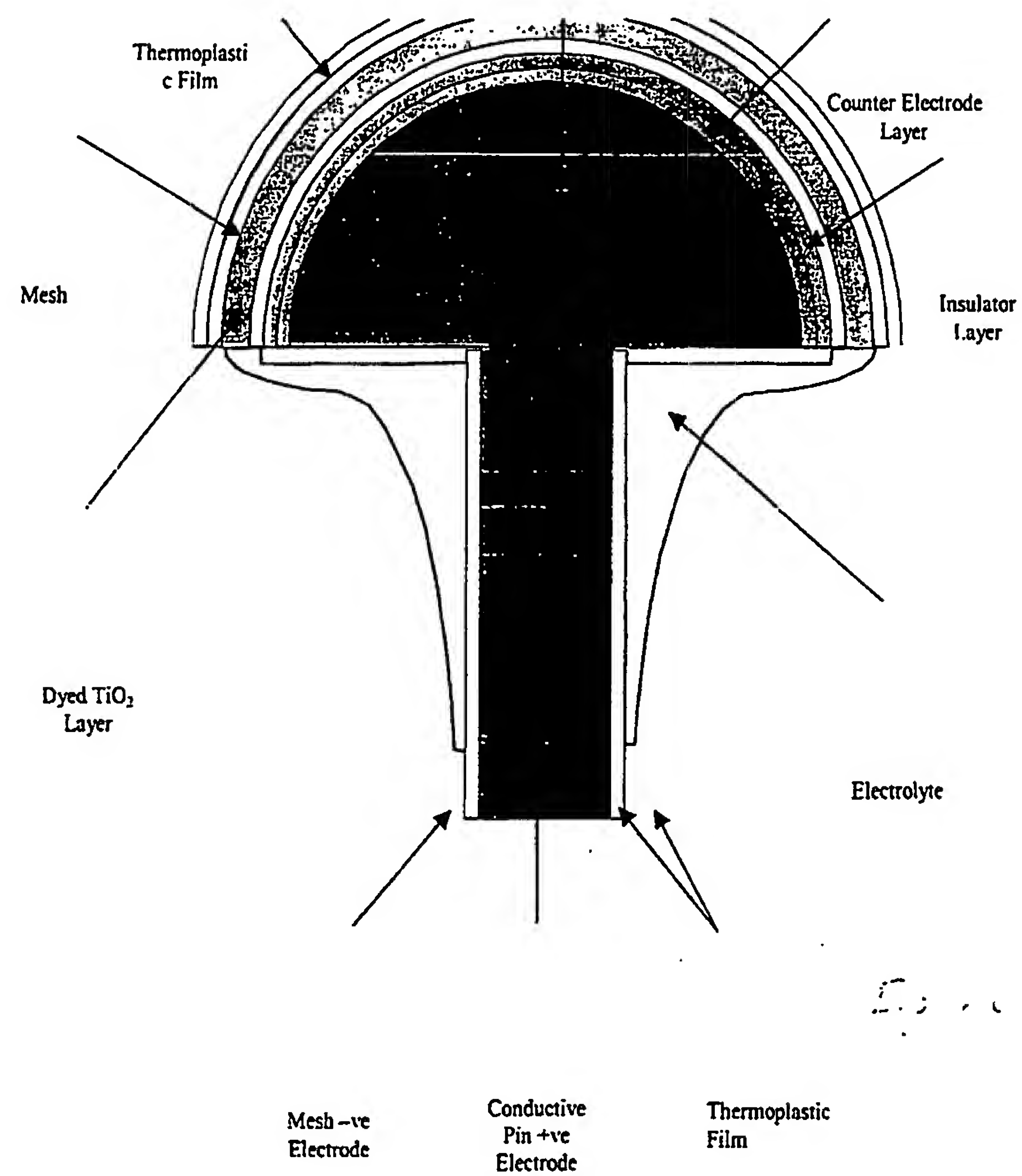

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